

Micro-Raman spectroscopic study of extremely large atmospheric ice conglomerations (megacryometeors)

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For the first time, micro-Raman spectroscopy has been applied to the structural study of four megacryometeors (extremely large atmospheric ice conglomerations that fall in general under blue-sky atmospheric conditions) that fell in Spain. The Raman spectra taken on the megacryometeor cores have been compared with those obtained from an *in situ* and online study performed on the crystallization process of water in the laboratory. A detailed comparison of the band profiles obtained made it possible to place the formation of the megacryometeors within a particular range of temperatures (−10 to −20°C), which in turn can be related with the altitude of formation in the atmosphere. These results have also been compared with isotope concentrations ($\delta^{18}\text{O}$ and δD) previously obtained in these cores. The two sets of results show a close correlation.

Keywords: megacryometeors; Raman spectroscopy; ice formation

1. Introduction

Water is the only substance that can exist in all three phases (gas, liquid and solid (ice)) in the atmosphere (Turner & Whiteman 2002). Vibrational spectroscopic techniques and, particularly, Raman spectroscopy are very well suited for studying the different structural situations of water (Walrafen 1964; Kamb 1968; Scherer *et al.* 1974; Rull 2002). More than 6700 scientific papers (ISI-Web of Science database) relating Raman and water have been published during the last half century and, since the famous paper by Leonard (1967), regarding the observation of Raman scattering from the atmosphere using a pulsed nitrogen ultraviolet laser, more than 1000 articles have connected this extremely useful and versatile technique with atmospheric studies. However, the application of micro-Raman spectroscopy to the direct study of atmospheric ice conglomerations (e.g. hailstones) is, paradoxically, extremely scarce.

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Megacryometeors are large atmospheric ice conglomerations that, despite sharing many of the textural, hydrochemical and isotopic features detected in large hailstones, are formed under unusual atmospheric conditions that clearly differ from those of the cumulonimbus clouds scenario (i.e. clear-sky conditions) (Martínez-Frías & Travis 2002). Megacryometeors are neither classical big hailstones, ice from aircraft (waste water or tank leakage) nor a simple result of icing processes at high altitudes. A detailed historical review of such ice fall events confirms that there are many documented references of falls of large blocks of ice, which go back to the first half of the 19th century (prior to the invention of aircraft).

Previous contributions to the knowledge of megacryometeors have focused on the study of their textures (zones of ‘massive ice’, large isolated cavities, millimetre-sized oriented air bubbles and ice layering) and their hydrochemistry and isotopic composition, all of them evidencing a complex history of growth in the atmosphere (Martínez-Frías *et al.* 2000, 2001, 2005; Santoyo *et al.* 2002; Martínez-Frías & Delgado 2006; Orellana *et al.* 2008). To the best of our knowledge, no spectroscopic studies have been performed on these megacryometeors.

Given these features, in this paper, a micro-Raman study was carried out focused on the investigation of ice samples from four selected megacryometeor specimens that fell in Spain: Alcudia, Chilches, Enguera and Tocina.

These spectra were compared with those obtained in laboratory conditions on water vapour deposition samples and small liquid water samples cooled at different temperatures. The purpose of such a comparison was to get a possible correlation between the vibrational features of the OH stretching band in the megacryometeors and in the water crystallized at several temperatures.

2. Experimental details

Megacryometeor samples were collected under controlled conditions. The ice blocks were kept in aseptic bags and immediately stored under refrigeration at approximately -20°C , to avoid textural changes, as well as to prevent possible contamination on the surface of the megacryometeors by water–steam condensation, or by the absorption of carbon dioxide from the environment.

Samples were analysed in the two weeks after falling, and no structural modifications were expected to occur inside the samples. Micro-Raman spectroscopy was performed using a Spex M270 monochromator illuminated with an Ar^+ ion laser at 514.5 nm and using low power on the sample to avoid structural perturbations of the ice. The Raman system was coupled to a microscope through a Jobin-Yvon optical head and optical fibres. Detection was performed using an air-cooled charge-coupled device of 1024×512 pixels.

Spectra of water, under different cooling conditions down to -50°C , were also obtained with the same Raman system and a small chamber cooled with liquid nitrogen in which different surfaces or small containers can be located on the cold finger to carry out the cooling or heating process. The exciting laser is focused on the liquid water sample through a window, which in turn is isolated from the sample and the ambient air using a small laminar flow of nitrogen gas to avoid water condensation in the window.



Figure 1. A chunk of ice that fell in Chilches (Castellón de la Plana, Spain) having a diameter of around 10 cm.

Two types of experiments were performed starting from liquid or vapour. In the latter case, the series of spectra were less reliable than in the former owing to experimental difficulties with the cooling chamber. In the present paper, comparison is shown between megacryometeor spectra and liquid water cooled spectra at different rates of $2^{\circ}\text{C min}^{-1}$ and spectra taken at intervals of 60 s and $7^{\circ}\text{C min}^{-1}$ and spectra taken at intervals of 30 s. The spectra were also recorded on heating the ice formed in order to compare the band profile behaviour on cooling or heating at the same temperatures.

3. Results and discussion

In figure 1, a chunk of ice (megacryometeor) of about 10 cm diameter that fell in Chilches (Castellon, Spain) is shown. In figure 2, the Raman spectra of megacryometeors from Alcudia (AL), Enguera (ENG), Tocina (TO) and Chilches (CHIL) are shown in the spectral region of $1700\text{--}3700\text{ cm}^{-1}$. The main features observed in these spectra correspond well with those observed in ice Ih (Whalley 1977). The position of the prominent narrow band characteristic associated with the in-phase OH stretching vibrations of water appears at $3127\text{--}3130\text{ cm}^{-1}$, the bending water mode is practically absent and the broad features at high wavenumbers currently associated with out-of-phase vibrations of water (ν_3 TO and LO modes) appears at nearly constant position of 3260 and 3350 cm^{-1} , respectively.

The broad feature between the wavenumbers 1900 and 2800 cm^{-1} currently assigned to the combination bands with vibrational modes in liquid water and ice varies strongly from one sample to another.

The evolution of the Raman spectra of liquid water on cooling at a rate of $2^{\circ}\text{C min}^{-1}$ from 25 to -50°C is shown in figure 3. Spectra were normalized to unity in intensity for clarity in their interpretation. The main vibrational

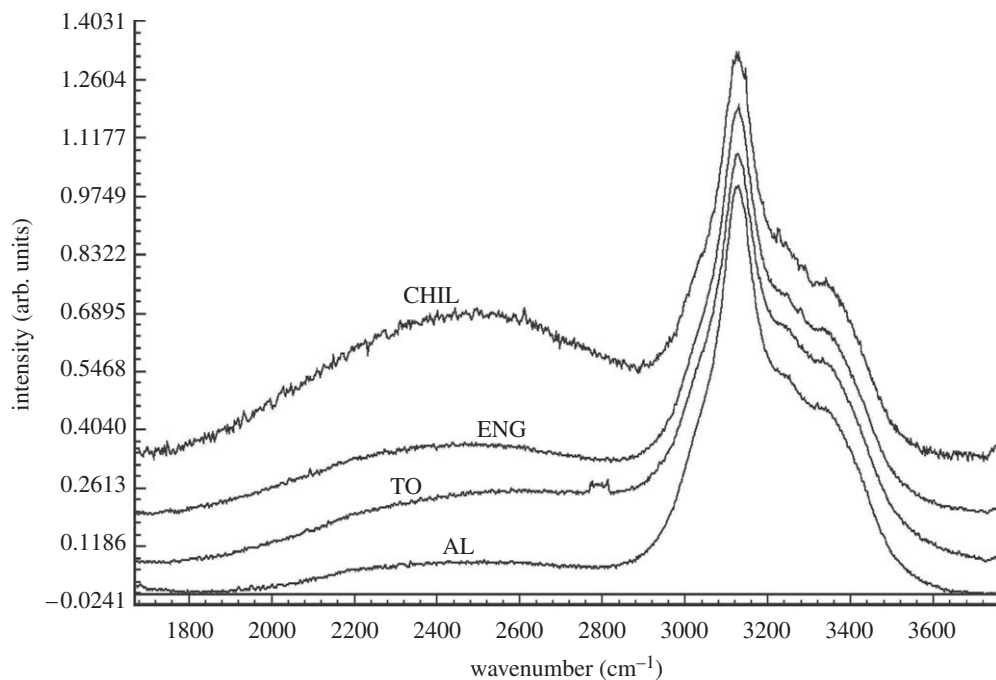


Figure 2. Raman spectra obtained at the centre of four megacryometeors that fell in Spain. AL, Alcudia; CHIL, Chilches; ENG, Enguera; TO, Tocina.

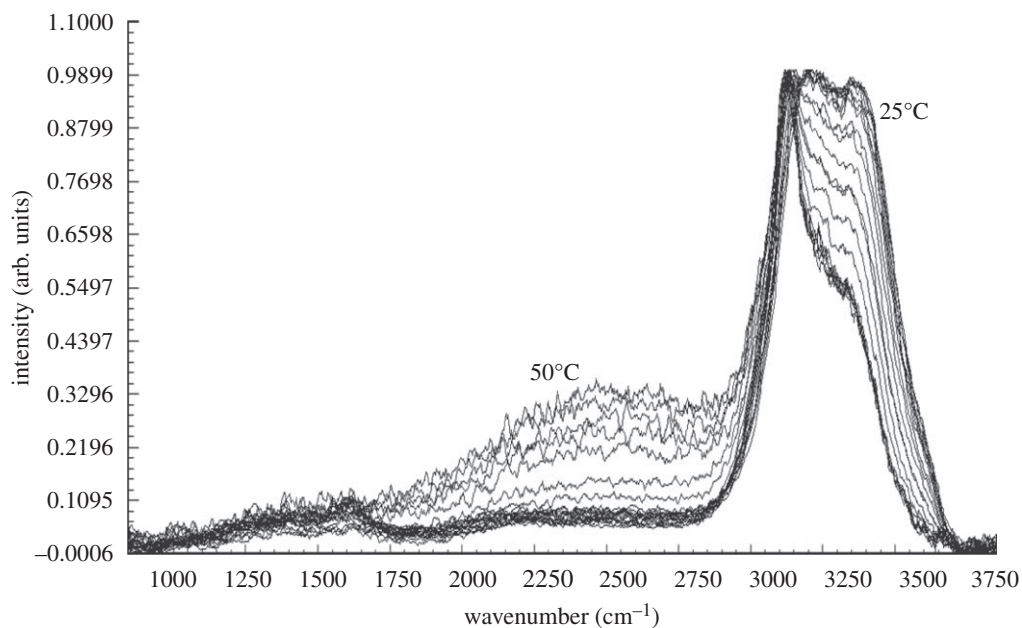


Figure 3. Raman spectra obtained at intervals of 60 s on cooling distilled water from 25 to -50°C at a rate of $2^{\circ}\text{C min}^{-1}$. The acquisition time of each spectrum was 10 s.

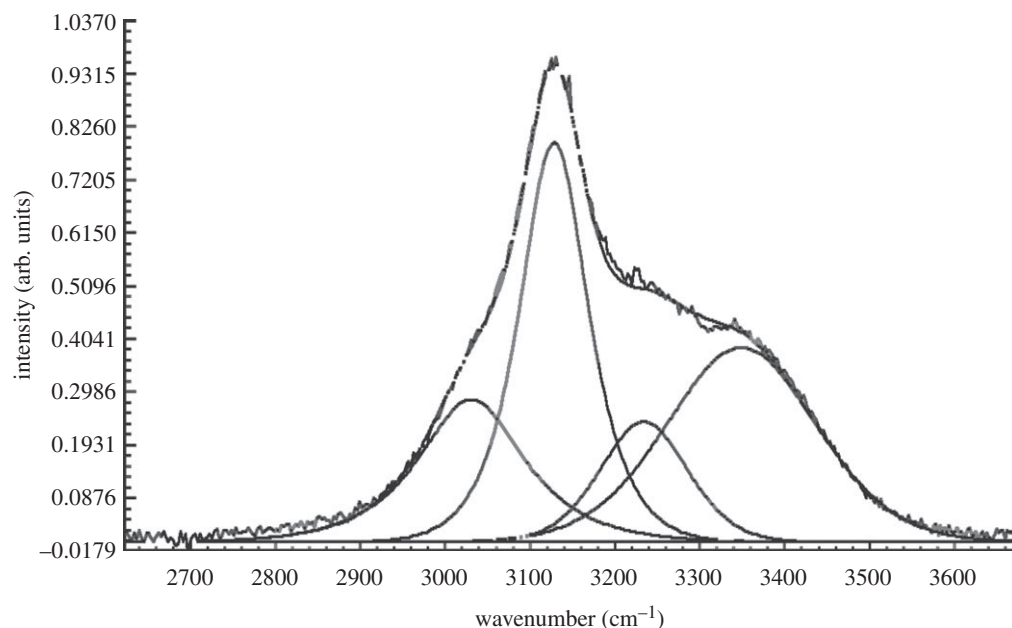


Figure 4. Band fitting performed on the Raman OH stretching band obtained from the Chilches sample. Four bands are obtained after deconvolution and subtraction of the broad feature covering the spectral range of 1900–2800 cm^{-1} .

characteristics of ice Ih can easily be seen, i.e. strong diminution of the main component at 3430 cm^{-1} and narrowing of the band at 3200 cm^{-1} . All the bands shift the position to low wavenumbers, giving a measured value of 3350 cm^{-1} at -50°C for the broad feature at high wavenumbers, and a value of 3116 cm^{-1} for the narrow feature at low wavenumbers. It is also interesting to note the decrease in intensity of the bending mode from liquid to ice. Finally, the very broad feature ranging from 1900 to 2800 cm^{-1} noticeably increases its intensity on cooling ice from about -10°C .

Comparison of the vibrational features observed in the megacryometeors and those observed on cooling liquid water has been performed using the normalized spectra. A detailed fitting of the band profile allows the different megacryometeor spectra to be placed in the range of those ice spectra at temperatures between -15°C and -20°C (figures 4 and 5). The band positions of the components match both systems with precision at these temperatures, and the widths were also very similar. Nevertheless, some differences were observed between the two profiles, which mostly affect the high-wavenumber band at 3355 cm^{-1} . These differences probably show that the kinetics of formation is different.

These data are close to those obtained from the isotopic ratio measurements. Isotopic studies of megacryometeors (Martínez-Frías *et al.* 2005; Martínez-Frías & Delgado 2006; Orellana *et al.* 2008) confirmed that $\delta^{18}\text{O}$ and δD (Vienna Standard Mean Ocean Water, V-SMOW) of all samples fall into the Meteoric Water Line (MWL), demonstrating unequivocally that megacryometeors match well with typical tropospheric values (figure 6). The most positive values

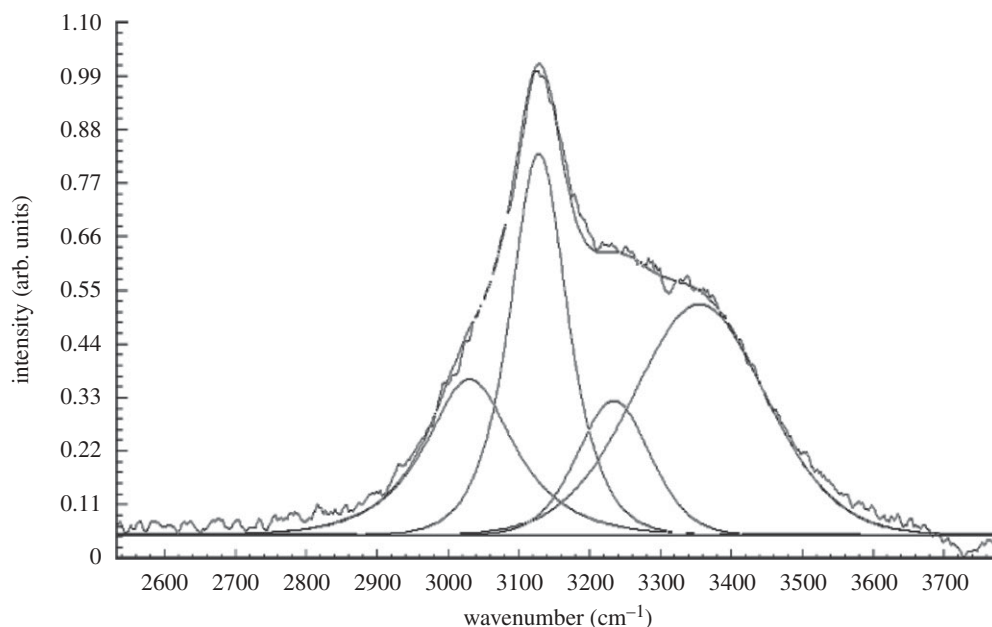


Figure 5. Band fitting performed on the Raman OH stretching band obtained at -20°C on cooling distilled water. Four bands are also obtained after deconvolution and subtraction of the broad feature covering the spectral range of $1900\text{--}2800\text{ cm}^{-1}$.

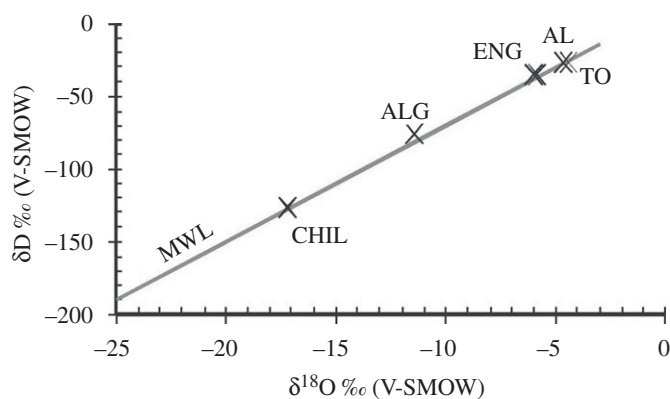


Figure 6. Measured $\delta^{18}\text{O}$ (V-SMOW) versus δD (V-SMOW) values of selected megacryometeors that fell in different areas of Spain and analysed in this work. The samples match quite well with the Meteoric Water Line (Craig's Line): $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$. CHIL, Chilches; ALG, Algemesi; ENG, Enguera; AL, Alcudia; TO, Tocina. (Adapted from Martínez-Frías *et al.* 2005.)

are typical of rain water in the Iberian Peninsula (e.g. Alcudia, Tocina). Relatively negative isotopic values for the middle latitudes were detected in some megacryometeors (e.g. Chilches, Castellon province) ($\delta^{18}\text{O} = -17.2\text{‰}$ and $\delta\text{D} = -127\text{‰}$ V-SMOW).

Table 1. Isotopic composition of megacryometeors (Spain). AL, Alcudia; CHIL, Chilches; ENG, Enguera; TO, Tocina.

Sample	$\delta^{18}\text{O}$ ‰ (V-SMOW)	δD ‰ (V-SMOW)
AL	4.99	25.7
CHIL	17.25	127.1
ENG	6.29	35.5
TO	4.52	27.3

Although the spectral features in the OH stretching region are not very different among the megacryometeors observed, two groups can be established. Alcudia, Tocina and Enguera behave very closely and spectral differences are very small. Chilches, in addition to a strong combination broadband feature in the 1900–2800 cm^{-1} spectral region, shows a small shift to low wavenumber and narrow bands. These two behaviours are also very close to those observed from isotopic ratio measurements (table 1).

We can conclude from this first micro-Raman analysis performed on megacryometeors that the Raman technique is very well suited to investigate the structural characteristics induced in ice during the process of crystallization. The changes associated with the ice formation history are reflected in the spectra as well as in the isotopic composition. Future work includes more precise cooling studies using different types of rain water and more detailed micro-Raman studies including detailed mapping of the megacryometeor cores.

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